Preparation and Characterization of Inclusion Complexes of Poly(dimethylsiloxane)s with Cyclodextrins

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ABSTRACT: β-Cyclodextrin (β-CD) and γ-cyclodextrin (γ-CD) formed inclusion complexes with poly(dimethylsiloxane)s (PDMS) of various molecular weights to give crystalline compounds. However, α-cyclodextrin (α-CD) did not form complexes with PDMS of any molecular weight. The yields of the β-CD−PDMS inclusion complexes decreased with increasing molecular weight of PDMS. In contrast, the yields of the γ-CD−PDMS inclusion complexes increased with increasing molecular weight, reached a maximum at molecular weight of around 760, and gradually decreased at higher molecular weight. The chain-length selectivity is reversed between β-CD and γ-CD. The β-CD−PDMS inclusion complexes are stoichiometric 1:1 compounds when the molecular weights of PDMS are low. The γ-CD−PDMS inclusion complexes are stoichiometric 2:3 (cyclodextrin:monomer unit of PDMS) compounds. The complexes were isolated and characterized by ^{1}H NMR, ^{13}C CP/MAS NMR, and X-ray diffraction studies. The inclusion modes are discussed.

Introduction

Cyclodextrins (CDs) are a series of cyclic oligosaccharides consisting of six to eight glucose units linked by α-1,4 linkages. They are called α-, β-, and γ-CD, respectively. CDs adopt a truncated conical structure, having the primary hydroxyl groups on the narrow (primary) side and the secondary hydroxyl groups on the wide (secondary) side. They are known to form inclusion complexes with various low molecular weight compounds. Since the discovery of cyclodextrins, there have been many reports on complex formation of cyclodextrins with small molecules and ions.[1−5]

Previously, we have reported that CDs form inclusion complexes with some organic polymers to give crystalline compounds with high selectivity. CDs form inclusion complexes not only with hydrophilic polymers but also with hydrophobic polymers (Table 1). For example, α-CD forms complexes with poly(ethylene glycol),[6−8] polyethylene (MW < 1000),[9] and some polyesters.[10,11] β-CD formed complexes with poly(propylene glycol)[12,13] and polypropylene (MW < 1000). γ-CD formed complexes with poly(methyl vinyl ether)[14,15] and polyisobutylene.[9,16,17] Other groups also reported complex formation between CDs and polyesters.[18−20] We also prepared a polyrotaxane in which many α-CDs were threaded onto a poly(ethylene glycol) chain.[21−23] Wenz et al. also reported α-CDs threaded on a polyamine.[24] All the complexes mentioned above are main chain polyrotaxanes, composed of CDs and organic polymers.

Recently, some inorganic polymers have attracted much attention, because they have excellent features such as resistance to heat and some chemicals. However, some of them are decomposed by oxidation, hydrolysis, and acid−base reactions. Silicon-containing polymers are exceptionally thermally and chemically stable.[25,26] Polyorganosiloxanes form a class of commercially important materials known as silicones. Poly(dimethylsiloxane) (PDMS) is the most common of the industrial silicone polymers. PDMS is unique because, despite high heat-stability, it is an oily material.

Recently, much attention has been focused on the design and construction of nanometer scale structures based on supramolecular noncovalent assemblies between organic compounds and inorganic materials called “organic−inorganic hybrids”. An example is the interpenetrating polymer hybrids constructed from silica gel and some polar organic polymers. However, these hybrids do not have strictly regulated structures. When inclusion complexes of CDs with PDMS are formed, they are new organic−inorganic hybrids with exact stoichiometric relationships. This paper describes the preparation and characterization of inclusion complexes of CDs with PDMS, and the modes of inclusion are discussed in detail.

Experimental Section

Materials. α-Cyclodextrin (α-CD) and γ-cyclodextrin (γ-CD) were kindly supplied by Nihon Shokuhinn Kako Co., Ltd. β-Cyclodextrin (β-CD) was obtained from Tokyo Kasei Kogyo Co., Ltd. Poly(dimethylsiloxane)s (PDMSs) were kindly supplied by Toray Dow Corning Silicone Co., Ltd and purchased from Shinetsu Kagaku Kogyo Co., Ltd.

Measurements. ^{1}H NMR spectra were recorded at 270 MHz on a JEOL EX-270 NMR spectrometer and at 400 MHz on a JEOL GSX-400 spectrometer at 30 °C. Chemical shifts were referenced to the solvent value ($\delta = 4.70$ ppm for D_2O, $\delta = 7.19$ ppm for pyridine-d_5, and $\delta = 7.26$ ppm for chloroform-d). ^{13}C NMR spectra were measured at 100.5 MHz on a JEOL GSX-400 spectrometer at 30 °C. Chemical shifts were referenced to the solvent value ($\delta = 77.0$ ppm for chloroform-d and $\delta = 123.5$ ppm for pyridine-d_5). ^{13}C-CP/MAS and ^{13}C-PST/MAS NMR spectra were measured at 75.6 MHz on a Chemagnetics JMN-CMX300W spectrometer with a sample spinning rate of 4.0 kHz at room temperature. Chemical shifts were referenced to external hexamethylbenzene ($\delta = 17.36$ ppm). Powder X-ray diffraction patterns were taken using Cu Kα irradiation with a Rigaku RAD-ROC X-ray diffractometer (voltage, 40 kV; current, 100 mA; scanning speed, 3 °C/min). FT-IR measurements were performed on a JASCO FT/IR-410 spectrometer. Gel permeation chromatography determination was carried out with Tohso CCP&8010 system (columns: G3000HXL and G2000HXL).

Calculation of Yields and Stoichiometries by ^{1}H NMR. The yields were calculated from the intensity ratio of the peaks

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Table 1. Complex Formation of CDs with Hydrophilic and Hydrophobic Polymers

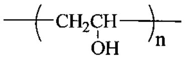
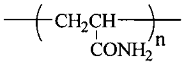
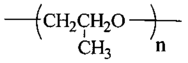
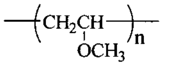
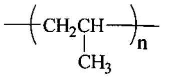
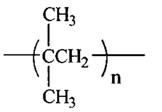
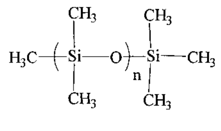
Polymer	Structure	$\overline{\mathrm{MW}}$	Yield(%)		
			α-CD	β-CD	γ-CD
PVA	 $\left(\mathrm{CH_2}\underset{\mathrm{OH}}{\mathrm{CH}}\right)_n$	22000	0	0	0
PAAm	 $\left(\mathrm{CH_2}\underset{\mathrm{CONH_2}}{\mathrm{CH}}\right)_n$	10000	0	0	0
PEG	$\left(\mathrm{CH_2CH_2O}\right)_n$	1000	92	0	trace
PPG	 $\left(\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{O}\right)_n$	1000	0	96	80
PMeVE	 $\left(\mathrm{CH_2}\underset{\mathrm{OCH_3}}{\mathrm{CH}}\right)_n$	2000	0	0	82
OE(20)	$\left(\mathrm{CH_2CH_2}\right)_n$	563	63	0	0
PP	 $\left(\mathrm{CH_2}\underset{\mathrm{CH_3}}{\mathrm{CH}}\right)_n$	ca.800	0	40	7
PIB	 $\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\right)_n$	ca.800	0	8	90

Table 2. Complex Formation Between PDMSs and CDs

Polymer	Structure	$\overline{M_n}$	$\overline{DP}$	Yield(%)[a]/Mole ratio[b]		
				α-CD	β-CD	γ-CD
PDMS	 $\mathrm{H_3C}\left(\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right)_n\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{CH_3}$	160	1	0	49 / 0.88	51 / 0.98
		240	2	0	68 / 1.3	58 / 1.3
		390	4	0	36 / 2.8	74 / 1.3
		760	9	0	a little	91 / 1.5
		1200	15	0	trace	81 / 1.5
		1900	24	0	0	82 / 1.4
		3200	42	0	0	72 / 1.5

[a] Based on CD. [b] Mole ratio of monomer unit PDMS to CD (calculated from the ^{1}H NMR spectra).

at 5.69 ppm derived from C_1H of CD and 0.14 ppm derived from the methyl proton of PDMS. Stoichiometry which means the ratio between CD and monomer units of polymer was calculated by the same manner as the determination of yield.

Preparation of *β*-CD—PDMS Inclusion Complexes. PDMS (29.8 mg, 4.03×10^{-4}mol) was put into a tube. A saturated aqueous solution of *β*-CD 14.7 mL containing 272 mg of *β*-CD (2.40×10^{-1} mol) was added at room temperature. The mixture was supersonically agitated for about 15 min and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation and dried under vacuum, then washed with THF and dried under vacuum, and finally washed with water and dried under vacuum to give the *β*-CD−PDMS complex. The results are summarized in Table 2.

***β*-CD—PDMS160.** Yield: 49%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.69 (d, 7H, C_1H of *β*-CD), 4.83 (t, 7H, C_3H of *β*-CD), 4.54 (m, 21H, C_5H and C_6H of *β*-CD), 4.31 (m, 7H, C_2H of *β*-CD), 4.15 (m, 7H, C_4H of *β*-CD), 0.117 (s, 18H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3435 (ν_s, O−H), 2928 (ν_s, C−H), 1254 (ν_{as}, Si−C), 1155, 1029 (ν_s, C−O), 1029 (ν_{as}, Si−O), 849 (ν_s, Si−C), 531 (ν_s, Si−O).

Anal. Calcd for $(C_{42}H_{70}O_{35})_{1.1}(C_6H_{18}OSi_2)_{1.0}(H_2O)_{7.2}$: C, 40.79; H, 7.13. Found: C, 40.77; H, 6.90.

***β*-CD—PDMS240.** Yield: 68%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.69 (d, 7H, C_1H of *β*-CD), 4.83 (t, 7H, C_3H of *β*-CD), 4.54 (m, 21H, C_5H and C_6H of *β*-CD), 4.31 (m, 7H, C_2H of *β*-CD), 4.15 (m, 7H, C_4H of *β*-CD), 0.203, 0.161 (m, 24H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3497(ν_s, OH), 2927 (ν_s, CH), 1259 (ν_{as}, Si−C), 1157, 1030 (ν_s, CO), 1030 (ν_{as}, Si−O), 847 (ν_s, Si−C), 579 (ν_s, Si−O).

Anal. Calcd for $(C_{42}H_{70}O_{35})_{1.5}(C_8H_{24}O_2Si_3)_{1.0}(H_2O)_{8.6}$: C, 40.80; H, 7.02. Found: C, 40.79; H, 6.93.

***β*-CD—PDMS390.** Yield: 36%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.68 (d, 7H, C_1H of *β*-CD), 4.83 (t, 7H, C_3H of *β*-CD), 4.54 (m, 21H, C_5H and C_6H of *β*-CD), 4.30 (m, 7H, C_2H of *β*-CD), 4.15 (m, 7H, C_4H of *β*-CD), 0.229, 0.205, 0.191 (m, 36H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3367 (ν_s, OH), 2928 (ν_s, CH), 1254 (ν_{as}, Si−C), 1157, 1030 (ν_s, CO), 1030 (ν_{as}, Si−O), 846(ν_s, Si−C), 529(ν_s, Si−O). Anal. Calcd for $(C_{42}H_{70}O_{35})_{2.4}(C_{12}H_{36}O_4Si_5)_{1.0}(H_2O)_{15.5}$: C, 40.03; H, 6.98. Found: C, 39.99; H, 7.03.

Preparation of *γ*-CD—PDMS Inclusion Complexes. PDMS (29.2 mg, 3.95×10^{-4} mol) was put into a tube. A saturated aqueous solution of *γ*-CD 1.34 mL containing 311 mg of *γ*-CD (2.40×10^{-1} mol) was added at room temperature. The mixture was supersonically agitated for about 15 min and then allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation and dried under vacuum, then washed with THF and dried under vacuum, and finally washed with water and dried under vacuum to give the *γ*-CD−PDMS complex. The results are summarized in Table 2.

***γ*-CD—PDMS160.** Yield: 51%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.72 (d, 8H, C_1H of *γ*-CD), 4.64 (t, 8H, C_3H of *γ*-CD), 4.37 (m, 24H, C_5H and C_6H of *γ*-CD), 4.28 (m, 8H, C_2H of *γ*-CD), 4.09 (m, 8H, C_4H of *γ*-CD), 0.116 (s, 18H, methyl H of PDMS). FT−IR (KBr, cm-1): 3390 (ν_s, O−H), 2929 (ν_s, C−H), 1254 (ν_{as}, Si−C), 1157, 1025 (ν_s, C−O), 1025 (ν_{as}, Si−O), 807 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{1.0}(C_6H_{18}OSi_2)_{1.0}(H_2O)_{10}$: C, 39.50; H, 7.25. Found: C, 39.42; H, 7.08.

***γ*-CD—PDMS240.** Yield: 58%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C_1H of *γ*-CD), 4.63 (t, 8H, C_3H of *γ*-CD), 4.38 (m, 24H, C_5H and C_6H of *γ*-CD), 4.27 (m, 8H, C_2H of *γ*-CD), 4.09 (t, 8H, C_4H of *γ*-CD), 0.230, 0.205, 0.191 (m, 24H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390 (ν_s, O−H), 2929 (ν_s, C−H), 1259 (ν_{as}, Si−C), 1158, 1027 (ν_s, C−O), 1027 (ν_{as}, Si−O), 807 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for

$(C_{48}H_{80}O_{40})_{1.5}(C_8H_{24}O_2Si_3)_{1.0}(H_2O)_{15}$: C, 39.28; H, 7.13. Found: C, 39.33; H, 6.98.

γ-CD—PDMS390. Yield: 74%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.70 (d, 8H, C_1H of γ-CD), 4.63(t, 8H, C_3H of γ-CD), 4.38(m, 24H, C_5H and C_6H of γ-CD), 4.27(m, 8H, C_2H of γ-CD), 4.09(t, 8H, C_4H of γ-CD), 0.230, 0.209, 0.191(m, 36H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390(ν_s, O−H), 2929(ν_s, C−H), 1260(ν_{as}, Si−C), 1157, 1026(ν_s, C−O), 1026(ν_{as}, Si−O), 802(ν_s, Si−C), 526(ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{3.1}(C_{12}H_{36}O_4Si_3)_{1.0}(H_2O)_{12}$: C, 41.77; H, 6.72. Found: C, 41.71; H, 6.74.

γ-CD—PDMS760. Yield: 91%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C_1H of γ-CD), 4.63 (t, 8H, C_3H of γ-CD), 4.38 (m, 24H, C_5H and C_6H of γ-CD), 4.27 (m, 8H, C_2H of γ-CD), 4.09(t, 8H, C_4H of γ-CD), 0.275, 0.221, 0.202 (m, 66H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390 (ν_s, O−H), 2929 (ν_s, C−H), 1254 (ν_{as}, Si−C), 1157, 1025 (ν_s, C−O), 1025 (ν_{as}, Si−O), 807 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{6.0}(C_{22}H_{66}O_9Si_{10})_{1.0}(H_2O)_{36}$: C, 40.53; H, 6.78. Found: C, 40.53; H, 6.77.

γ-CD—PDMS1200. Yield: 81%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C_1H of γ-CD), 4.63 (t, 8H, C_3H of γ-CD), 4.38 (m, 24H, C_5H and C_6H of γ-CD), 4.26 (m, 8H, C_2H of γ-CD), 4.08 (t, 8H, C_4H of γ-CD), 0.312, 0.233, 0.211 (m, 102H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390 (ν_s, O−H), 2929 (ν_s, C−H), 1261 (ν_{as}, Si−C), 1156, 1079, 1027 (ν_s, C−O), 1027 (ν_{as}, Si−O), 796 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{10}(C_{34}H_{102}O_{15}Si_{16})_{1.0}(H_2O)_{51}$: C, 40.91; H, 6.71. Found: C, 40.93; H, 6.70.

γ-CD—PDMS1900. Yield: 82%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C_1H of γ-CD), 4.63 (t, 8H, C_3H of γ-CD), 4.38 (m, 24H, C_5H and C_6H of γ-CD), 4.26 (m, 8H, C_2H of γ-CD), 4.08 (t, 8H, C_4H of γ-CD), 0.327, 0.283, 0.237, 0.219 (m, 156H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390 (ν_s, OH), 2929 (ν_s, CH), 1262 (ν_{as}, Si−C), 1157, 1025 (ν_s, CO), 1025 (ν_{as}, Si−O), 796 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{17}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{68}$: C, 41.48; H, 6.62. Found: C, 41.48; H, 6.70.

γ-CD—PDMS3200. Yield: 72%. ^{1}H NMR (pyridine-d_5, 270 MHz): δ 5.71 (d, 8H, C_1H of γ-CD), 4.63 (t, 8H, C_3H of γ-CD), 4.38 (m, 24H, C_5H and C_6H of γ-CD), 4.26 (m, 8H, C_2H of γ-CD), 4.08 (t, 8H, C_4H of γ-CD), 0.335, 0.242, 0.227 (m, 18H, methyl H of PDMS). FT−IR (KBr, cm^{-1}): 3390 (ν_s, O−H), 2929 (ν_s, C−H), 1262 (ν_{as}, Si−C), 1156, 1026 (ν_s, C−O), 1026 (ν_{as}, Si−O), 796 (ν_s, Si−C), 526 (ν_s, Si−O). Anal. Calcd for $(C_{48}H_{80}O_{40})_{28}(C_{52}H_{156}O_{24}Si_{25})_{1.0}(H_2O)_{126}$: C, 41.16; H, 6.65. Found: C, 41.16; H, 6.73.

Continuous Variation Method. PDMSs and aqueous solutions of CDs were put into tubes. The total amount of repeat unit of PDMSs and CDs was fixed at 4.8×10^{-4} mol (β-CD−PDMS) or 7.0×10^{-4} mol (γ-CD−PDMS), while the molar fractions of CDs were varied from 0 to 1.00. The mixture was supersonically agitated for about 15 min and allowed to stand overnight at room temperature. The precipitated product was collected by centrifugation, dried under vacuum, washed with water and dried under vacuum, and then washed with THF and dried under vacuum.

Preparation of PDMS—TPAA. Triphenylacetic acid (TPAA) (2.16 g, 7.48×10^{-3}mol) was put into the Schlenk tube. Thionyl chloride (53.0 g, 0.445 mol) was poured upon the sample and refluxed over 8 h. After the reaction, excess amount of thionyl chloride was removed by trap-to-trap distillation. Then, dried pyridine was put onto the reaction products at 0 °C. Bis(3-aminopropyl)poly(dimethylsiloxane) (MW = 870) (2.51 g, NH_2, 5.76×10^{-3}mol) was added into the reaction tube, and stirred for 9 h. Reaction mixture was separated by alumina column chromatography (50 × 150 mm, Merck aluminum oxide 150 basic typT, ethyl acetate 100%) and size exclusion chromatography (22 × 880 mm, Sephadex LH-20, THF). Yield: 2.16 g (63.6%) ^{1}H NMR (THF-d_8, 400 MHz): δ 7.20, 7.22, 7.25 (m, 30H, H of phenyl ring of TPAA), 4.67 (s, 2H, NH of amide bond), 0.413, 1.48, 3.21 (m, 12H, CH_2 of PDMS), 0.056, 0.071, 0.106 (m, 72H, methyl H of PDMS). ^{13}C NMR (chloroform-d, 100.4 MHz): δ 173 (C of amide bond), 126, 128, 131, 144 (C of phenyl ring of TPAA), 67.8 (C of TPAA), 15.3, 23.2, 43.0 (CH_2 of PDMS), 0.061, 1.01, 1.12 (CH_3 of PDMS). FT−IR (KBr, cm^{-1}): 3298 (ν_s, N−H), 2927 (ν_s, C−H), 1642 (δ_{as}, NH and ν_s, C=O), 1451 (ν_s, C−N), 1260 (ν_{as}, Si−C), 1024 (ν_{as}, Si−O), 801 (ν_s, Si−C). Anal. Calcd for $C_{48}H_{122}N_2O_{14}Si_{13}$: C 53.89; H 7.66; N 1.75. Found: C 53.94; H 7.62; N 1.80.

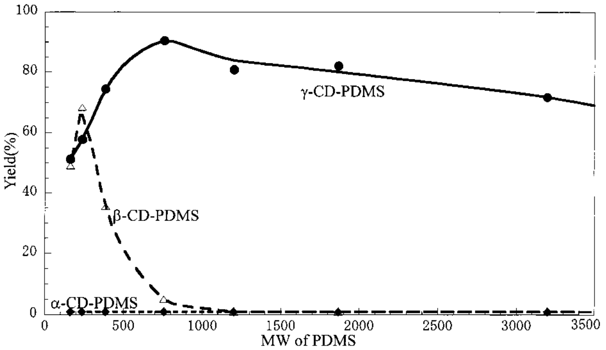


Figure 1. Yields of CD−PDMS complexes as a function of the molecular weight of PDMS.

Calculation of Yields and Stoichiometries by ^{1}H NMR. The yields were calculated from the intensity ratio of the peaks at 5.69 ppm derived from C_1H of CD and 0.14 ppm derived from the methyl proton of PDMS. Stoichiometry, which means the ratio between CD and monomer units of polymer, was calculated by the same manner as the determination of yield.

Results and Discussion

Complex Formation of CDs with PDMSs. When PDMS (liquid) was added to aqueous solutions of β-CD (diameter of the cavity: 7.0 Å) or γ-CD (diameter of the cavity: 8.5 Å) and the mixture was sonicated at room temperature for 10 min, the heterogeneous solution became turbid and the complexes were formed as crystalline precipitates. This is the first observartion that cyclodextrins formed a complex with inorganic polymers. However, α-CD did not form complexes with PDMS. Table 2 shows the results of the complex formation between CDs and PDMS. β-CD and γ-CD formed complexes with PDMS, although α-CD did not give complexes with PDMS of any molecular weight. The cavities of β-CD and γ-CD are large enough to accommodate PDMS. However, the α-CD cavity (diameter of the cavity: 4.5 Å) is too small for PDMS to penetrate due to steric hindrance by dimethyl groups on the main chain. These results indicate that the relative sizes of the cavities of cyclodextrins to the cross-sectional area of the polymers are important in the complex formation of polymers with cyclodextrins. Thus, cyclodextrins recognize the diameter of polymer chains. These phenomena are similar to those of the complex formation of CDs with polyisobutylene.[14,15] But these results are the first example of molecular level "organic−inorganic hybrids" using host−guest complexation.

When PDMSs were added to the solution of CDs in DMF and DMSO, the mixture did not change and no precipitate was formed. This result indicates that hydrophobic interaction is also important to form complexes of CDs with PDMS.

Effects of the Molecular Weight on the Complex Formation. Figure 1 shows the yields of the complexes as a function of the molecular weight of PDMS. The yields are based on the starting amount of CD and the stoichiometry of CD to PDMS as described below, using saturated solutions of CD and PDMS (1.5 equiv monomer units to CD). The yields of the complexes of PDMS with γ-CD increased with increasing PDMS molecular

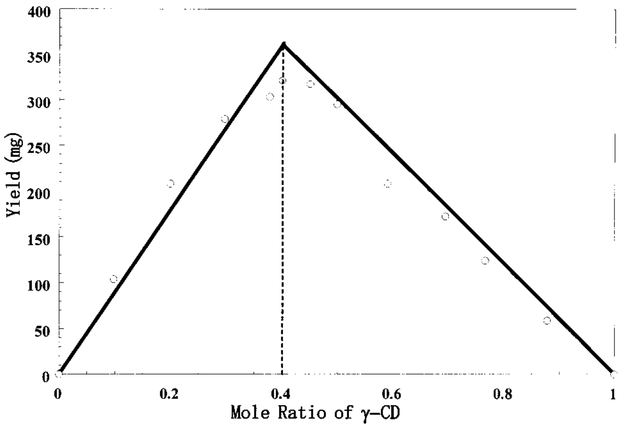


Figure 2. Continuous variation plots for γ-CD−PDMS1200 complexes. Total amount of γ-CD and siloxane unit of PDMS was fixed at 7.0×10^{-4}mol.

weight, reached a maximum at around $M_w = 760$, and then decreased (Figure 1). The complexes were obtained almost quantitatively with PDMS of molecular weights of 750 with γ-CD. In contrast, the yields of the complexes of PDMS with β-CD decreased with increasing PDMS molecular weight, although the yield of the complex between β-CD and PDMS (MW = 240) is lower than that of PDMS (MW = 400). The chain-length selectivities are reversed between β-CD and γ-CD. β-CD formed a complex with a dimer model compound, hexamethyldisiloxane (HMDS, MW = 162). β-CD forms 1:1 complexes with small molecules, which seem to be rather unstable compared to those complexes with long molecules which give higher order stoichiometries. The β-CD cavity is too small to diffuse onto a long PDMS chain, and interact strongly with PDMS through van der Waals interactions. α-CD did not form complexes with PDMS of any molecular weight.

Stoichiometries. The complex formation of γ-CD with PDMS was studied quantitatively. The yields of the complexes of γ-CD with PDMS increases with an increase in the amount of PDMS added to the aqueous solution of γ-CD, and a saturation was observed. This saturation behavior suggests that the complex formation is stiochiometric. Figure 2 shows a continuous variation plot (Job plot) for the formation of complexes of γ-CD with PDMS ($M_w = 760$). The plots show a maximum at 0.40 of molar fraction of γ-CD, indicating that γ-CD form complexes with PDMS with a 2:3 (γ-CD:monomer unit) stoichiometry; i.e., the cavity of a single cyclodextrin binds to 1.5 monomer units of PDMS.

The complexes were isolated by centrifugation and filtration and washed with tetrahydrofuran to remove nonincluded PDMS, dried, and then washed with water to remove uncomplexed CD and dried again. Figure 3 shows the ^{1}H NMR spectrum of the complex between γ-CD and PDMS of molecular weight of 1900. We calculated the mole ratio of PDMS to γ-CD in the complex. Comparing the integral of the peak of CD(1H) and that of the methyl group on PDMS, 1.5 monomer units were found to bind to a γ-CD molecule. The mole ratios of the complexes (monomer unit/γ-CD) are 1.5 in the range of $M_w = 700-3000$, which is similar to those obtained from the Job plots (Figure 2). The length of 1.5 monomer units corresponds to the depth of the γ-CD cavity.

Properties. The inclusion complexes were thermally stable. TG measurements of the complexes show that they decompose above 300 °C. The complexes were insoluble in water. When the complexes were added into boiling water, they decomposed into CD and PDMS. The addition of urea, which is thought to affect hydrogen bonds, to the suspension of the γ-CD−PDMS complex with heating resulted in solubilization of the complexes in water. This result indicates that hydrogen bonding between CDs plays an important role in stabilizing the complex. The complexes are soluble in dimethyl sulfoxide, dimethyl formamide, and pyridine. The X-ray diffraction studies (powder) show that all of the complexes are crystalline, although PDMS is a liquid.

Inclusion Modes of the Complexes. β-CD−PDMS and γ-CD−PDMS complexes are crystalline. Saenger

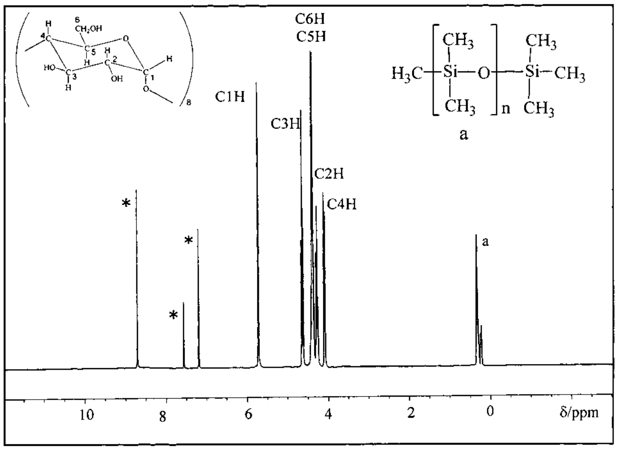


Figure 3. 270 MHz ^{1}H NMR spectrum of γ-CD−PDMS1900 complex in pyridine-d_5 at 30 °C.

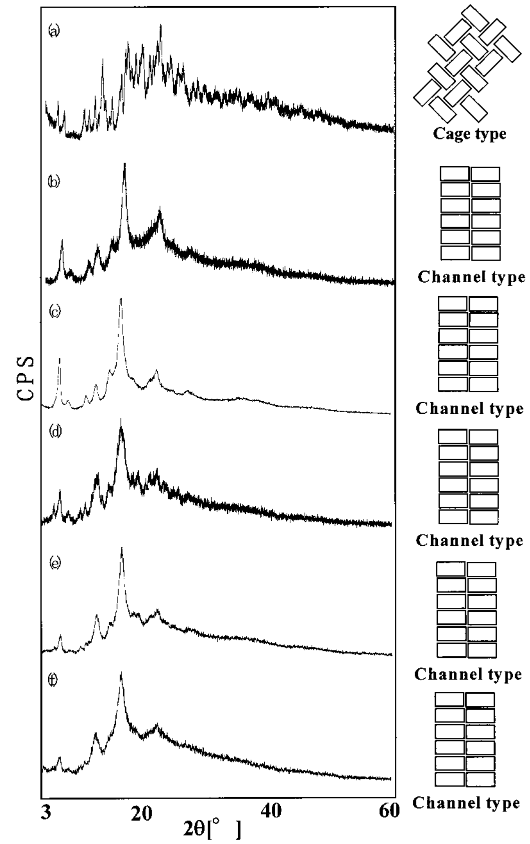


Figure 4. Powder X-ray diffraction patterns for (a) γ-CD, (b) γ-CD−PPG725, (c) γ−CD−PDMS160, (d) γ-CD−PDMS760, (e) γ-CD−PDMS1900, and (f) γ−CD−PDMS3200 complexes.

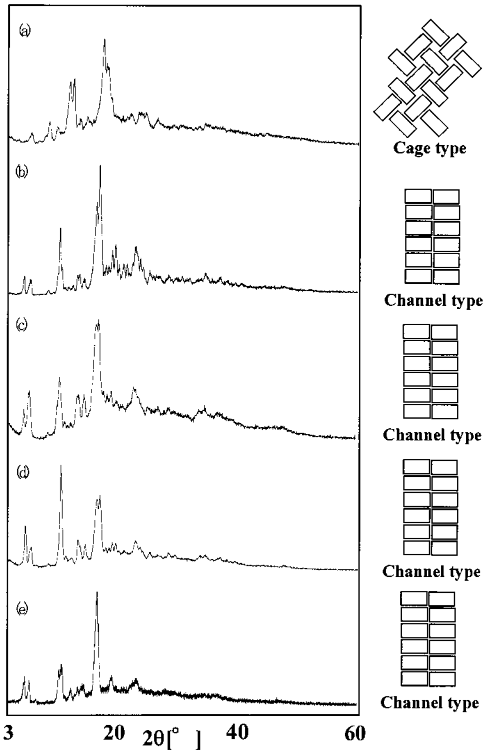


Figure 5. Powder X-ray diffraction patterns for (a) β-CD, (b) β–CD-*p*-nitroacetanilide, (c) β-CD–PDMS160, (d) β-CD–PDMS240, and (e) β–CD–PDMS390 complexes.

and Harata reported that the crystal structures of CD complexes are classified mainly into three types: channel-type, cage-type, and layer-type.[27–29] Figure 4 shows the powder X-ray diffraction patterns of γ-CD and γ-CD–PDMS complexes and the γ-CD–PPG complex. The γ-CD–PPG complex was found to adopt a head-to-head channel-type structure in which γ-CD molecules are stacked along a PPG axis to form a cylinder. The reflection peaks of γ-CD–PDMS complexes are similar to those of the γ-CD–PPG complex and different from those of γ-CD. These results suggest that γ-CD–PDMS complexes form head-to-head channels. Figure 5 shows the powder X-ray diffraction patterns of β-CD, β-CD-*p*-nitroacetanilide complex, and β-CD–PDMS complexes. β-CD-*p*-nitroacetanilide complex was found to adopt a head-to-head channel-type structure in which β-CD molecules are stacked along a PDMS axis to form a cylinder.[10,30] The reflection peaks of β-CD–PDMS complexes are similar to those of β-CD-*p*-nitroacetanilide complex, and different from those of β-CD. These results suggest that β-CD–PDMS complexes form head-to-head channels.

Solid-state ^{13}C NMR studies (such as ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR) give information about structures of CD complexes. Figure 6 shows the ^{13}C CP/MAS NMR spectra of γ-CD and γ-CD–PDMS complexes. The ^{13}C resonances of C(1) and C(4) of γ-CD gave multiplet lines because of the asymmetric glucopyranosyl conformations. However, the ^{13}C signals of C(1) and C(4) of γ-CD–PDMS complexes gave sharp singlets, showing that the γ-CD takes symmetric cyclic conformation. These results of solid-state ^{13}C NMR analysis supports the point that CDs form channel-type complexes with PDMS.

To study the effects of the end groups of PDMS on the complex formation, the complex formation between CDs and PDMS with various end groups was studied.

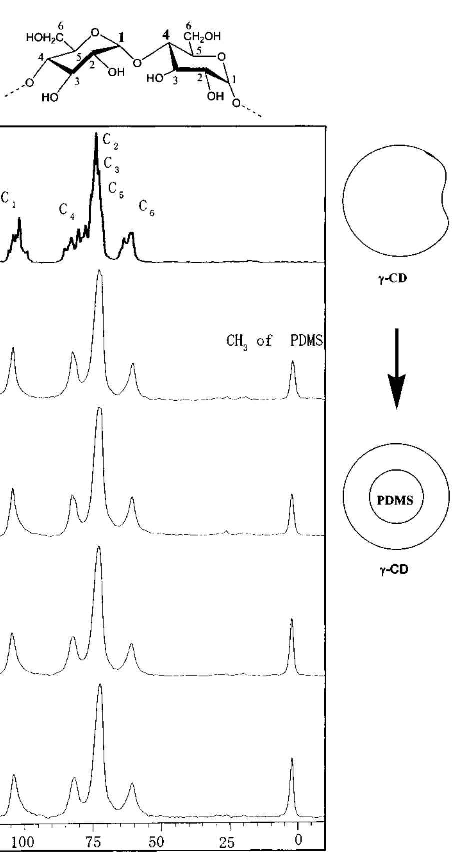
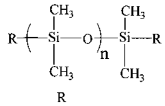


Figure 6. ^{13}C CP/MAS NMR spectra of (a) γ-CD, (b) γ-CD–PDMS760, (c) γ–CD–PDMS1200, (d) γ-CD–PDMS1900, and (e) γ-CD–PDMS3200 complexes.

Table 3. Complex Formation of CDs with Various End Groups

 R	$\overline{MW}$	$\overline{DP}$	Yield(%)[a)] / Mole ratio[b)]		
			α-CD	β-CD	γ-CD
$-C_3H_6NH_2$	248	1	0	68 / 0.57	75 / 0.75
	870	9	0	6 / 5.2	66 / 2.3
	1300	15	0	0	58 / 1.6
	4400	57	0	0	43 / 1.2
$-C_2H_4CO_2H$	1400	16	0	0	67 / 1.1
	1940	23	0	0	58 / 2.3
	4580	59	0	0	41 / 2.7
$-C_3H_6C_6H_4OH$	1500	17	0	0	66 / 1.3
	3000	37	0	0	62 / 1.8
$-C_3H_6OCH_2\underset{\diagdown O \diagup}{CH{-}CH_2}$	1300	14	0	0	62 / 1.7
$-H$	580	8	0	6 / 4.3	61 / 1.5
$-NHCO-C(C_6H_5)_3$	1600	12	0	0	0

[a] Based on CD. [b] Mole ratio of monomer unit PDMS to CD (calculated from the ^{1}H NMR spectra).

Table 3 shows the results of the complex formation between CDs and PDMS with various end groups. PDMS with small end groups such as amino and carboxyl groups formed complexes with γ-CD in high yields. However, PDMS having large substituents, such as trityl groups (PDMS–TPAA, M_w = 1600), did not form complexes with CDs. The bulky end groups seem to prevent the PDMS chain from penetrating the cavities of cyclodextrins.

Molecular model studies show that the PDMS chain is able to penetrate the γ-CD cavity, while the PDMS

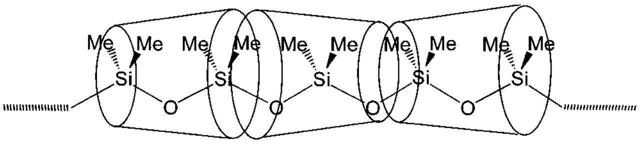


Figure 7. Proposed structure of γ-CD−PDMS760 inclusion complex.

chain cannot pass through the α-CD cavity owing to the hindrance of the dimethyl groups on the main chain. The hindrance of the dimethyl groups makes PDMS difficult to penetrate β-CD cavities. These views are in accordance with our results that γ-CD formed a complex with PDMS but α-CD did not form complexes with PDMS. Model studies further indicate that the single cavity accommodates 1.5 monomer units. Figure 7 shows a proposed structure of the complex of PDMS with γ-CD.

Conclusions

In conclusion, β-CD and γ-CD form complexes with PDMS, and α-CD did not form stoichiometric complexes with PDMS. β-CD and γ-CD form complexes with PDMS. This is the first observation that cyclodextrins formed a complex with inorganic polymers. The chain-length selectivities are totally different between β-CD and γ-CD. Studies of the detailed structures of the complexes are now in progress. These kinds of complexes may provide a new route to create new organic−inorganic hybrids and other functional supramolecular architectures.

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